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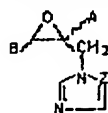
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Application Number:

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(54) INFLUENCING PLANT GROWTH BY MEANS OF  
AZOLYLMETHYLOXIRANES

(54) MODIFICATION DE LA CROISSANCE DE PLANTES A L'AIDE  
D'AZOLYLMETHYLOXIRANES


Representative Drawing:



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### ABSTRACT:

ABSTRACT OF THE DISCLOSURE: A method of influencing the growth of plants, wherein the soil, the seeds and/or the plants are treated with an azolymethyloxirane of the formula  (I), where A and B are each C1-C4-alkyl, phenyl, naphthyl, diphenyl or phenyl bearing from one to three substituents selected from the group consisting of halogen, C1-C4-alkyl, C1-C4-alkoxy, C1-C4-haloalkyl, nitro or phenoxy, and Z is CH or nitrogen, or a metal salt or acid addition salt thereof, and agents for influencing plant growth containing at least one azolymethyloxirane I.

CLAIMS: [Show all claims](#)

\*\*\* Note: Data on abstracts and claims is shown in the official language in which it was submitted.

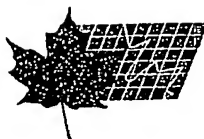
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MARQUES  
DE COMMERCE  
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(51) INTL.CL. <sup>5</sup> A01N-043/653; A01N-043/50

(19) (CA) CANADIAN PATENT (12)

(54) Influencing Plant Growth by Means of  
Azolylmethyloxiranes

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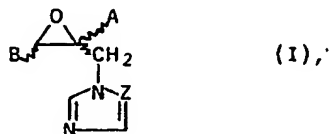
(57) 9 Claims

NO DRAWING



We claim:

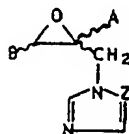
1. A process for influencing the growth of plants, wherein the soil, the seeds or the plants are treated with an azolymethyloxirane of the general formula I



- where A and B are each C<sub>1</sub>-C<sub>4</sub>-alkyl, phenyl, naphthyl, diphenyl or phenyl bearing from one to three substituents selected from the group consisting of halogen, C<sub>1</sub>-C<sub>4</sub>-alkyl, C<sub>1</sub>-C<sub>4</sub>-alkoxy, C<sub>1</sub>-C<sub>4</sub>-haloalkyl, nitro or phenoxy, and Z is CH or nitrogen, or a metal salt or acid addition salt thereof.
2. A process for influencing the growth of plants as set forth in claim 1, wherein the soil, the seeds or the plants are treated with from 0.1 to 95wt% of an azolymethyloxirane of the formula I, together with conventional carriers.
3. The use of azolymethyloxiranes of the general formula I as set forth in claim 1 for influencing plant growth.
4. A process for influencing the growth of plants, wherein the soil, the seeds or the plants are treated with an azolymethyloxirane of the general formula I as set forth in claim 1, where A is 4-fluorophenyl, B is 2-trifluoromethylphenyl and Z is nitrogen.
5. A process for influencing the growth of plants, wherein the soil, the seeds or the plants are treated with an azolymethyloxirane of the general formula I as set forth in claim 1, where A is 4-chlorophenyl, B is 4-trifluoromethylphenyl and Z is nitrogen.

Influencing plant growth by means of  
azolymethyloxiranes

The present invention relates to a method for influencing plant growth by treating the soil, the seed  
5 and/or the plants with an azolymethyloxirane of the general formula I



(I)

10

where A and B are identical or different and are each C<sub>1</sub>-C<sub>4</sub>-alkyl, phenyl, naphthyl or diphenyl or are each phenyl which is substituted by one radical, or two or three  
15 identical or different radicals, from the group consisting of halogen, C<sub>1</sub>-C<sub>4</sub>-alkyl, C<sub>1</sub>-C<sub>4</sub>-alkoxy, C<sub>1</sub>-C<sub>4</sub>-halo-alkyl, nitro and phenoxy, and Z is CH or nitrogen, or its metal salts or acid addition salts, and plant growth regulators containing a bioregulatory amount of an azolymethyl-  
20 oxirane I.

EP-A-94 564 discloses the azolymethyloxiranes of the general formula I; they are recommended for use as drugs, particularly as antimycotics, and as crop protection agents, especially as fungicides. No other uses of  
25 these compounds are known.

It is an object of the present invention to provide the azolymethyloxiranes for novel fields of use.

We have found that this object is achieved and that the azolymethyloxiranes I defined at the outset are  
30 suitable for regulating plant growth.

The substituents in formula I have the following specific meanings:

A and B independently of one another are each straight-chain or branched C<sub>1</sub>-C<sub>4</sub>-alkyl, such as methyl,  
35 ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl or tert-butyl,  
phenyl,



naphthyl, such as 1-naphthyl or 2-naphthyl, preferably 2-naphthyl,

diphenyl, such as o-diphenyl, m-diphenyl or p-diphenyl, phenyl which is substituted by one, two or three halogen

5 atoms, such as 2-fluorophenyl, 3-fluorophenyl, 4-fluorophenyl, 2-chlorophenyl, 3-chlorophenyl, 4-chlorophenyl, 2-bromophenyl, 3-bromophenyl, 4-bromophenyl, 2,3-difluorophenyl, 2,4-difluorophenyl, 2,5-difluorophenyl, 2,6-difluorophenyl, 3,4-difluorophenyl, 3,5-difluoro-

10 phenyl, 2,3-difluorophenyl, 2,4-dichlorophenyl, 2,5-dichlorophenyl, 2,6-dichlorophenyl, 3,4-dichlorophenyl, 3,5-dichlorophenyl, 2,3-dibromophenyl, 2,4-dibromophenyl, 2,5-dibromophenyl, 2,6-dibromophenyl, 3,4-dibromophenyl, 3,5-dibromophenyl, 2-chloro-3-fluorophen-

15 yl, 3-chloro-2-fluorophenyl, 2-chloro-4-fluorophenyl, 4-chloro-2-fluorophenyl, 2-chloro-5-fluorophenyl, 5-chloro-2-fluorophenyl, 2-chloro-6-fluorophenyl, 3-chloro-4-fluorophenyl, 4-chloro-3-fluorophenyl, 3-chloro-5-fluorophenyl, 2-bromo-3-fluorophenyl, 3-bromo-2-fluoro-

20 phenyl, 2-bromo-4-fluorophenyl, 4-bromo-2-fluorophenyl, 2-bromo-5-fluorophenyl, 5-bromo-2-fluorophenyl, 2-bromo-6-fluorophenyl, 3-bromo-4-fluorophenyl, 4-bromo-3-fluorophenyl, 3-bromo-5-fluorophenyl, 2-bromo-3-chlorophenyl, 3-bromo-2-chlorophenyl, 2-bromo-4-chlorophenyl, 4-bromo-

25 2-chlorophenyl, 2-bromo-5-fluorophenyl, 5-bromo-2-chlorophenyl, 4-bromo-6-chlorophenyl, 3-bromo-4-chlorophenyl, 4-bromo-3-chlorophenyl or 3-bromo-5-chlorophenyl, phenyl which is substituted by one, two or three C<sub>1</sub>-C<sub>4</sub>-alkyl groups,

30 phenyl which is substituted by one, two or three C<sub>1</sub>-C<sub>4</sub>-alkoxy groups,

phenyl which is substituted by one, two or three C<sub>1</sub>-C<sub>4</sub>-haloalkyl groups,

phenyl which is substituted by one or two nitro groups,

35 phenyl which is substituted by one, two or three phenoxy groups,

phenyl which is disubstituted or trisubstituted by

- halogen and C<sub>1</sub>-C<sub>4</sub>-alkyl,  
phenyl which is disubstituted or trisubstituted by halogen and C<sub>1</sub>-C<sub>4</sub>-alkoxy,  
phenyl which is disubstituted or trisubstituted by halogen and C<sub>1</sub>-C<sub>4</sub>-haloalkyl,  
5 phenyl which is disubstituted or trisubstituted by halogen and nitro,  
phenyl which is disubstituted or trisubstituted by halogen and phenoxy,  
10 phenyl which is disubstituted or trisubstituted by C<sub>1</sub>-C<sub>4</sub>-alkyl and C<sub>1</sub>-C<sub>4</sub>-alkoxy,  
phenyl which is disubstituted or trisubstituted by C<sub>1</sub>-C<sub>4</sub>-alkyl and C<sub>1</sub>-C<sub>4</sub>-haloalkyl,  
phenyl which is disubstituted or trisubstituted by C<sub>1</sub>-C<sub>4</sub>-alkyl and nitro,  
15 phenyl which is disubstituted or trisubstituted by C<sub>1</sub>-C<sub>4</sub>-alkyl and phenoxy,  
phenyl which is disubstituted or trisubstituted by C<sub>1</sub>-C<sub>4</sub>-alkoxy and C<sub>1</sub>-C<sub>4</sub>-haloalkyl,  
20 phenyl which is disubstituted or trisubstituted by C<sub>1</sub>-C<sub>4</sub>-alkoxy and nitro,  
phenyl which is disubstituted or trisubstituted by C<sub>1</sub>-C<sub>4</sub>-alkoxy and phenoxy,  
phenyl which is disubstituted or trisubstituted by C<sub>1</sub>-C<sub>4</sub>-haloalkyl and nitro,  
25 phenyl which is disubstituted or trisubstituted by C<sub>1</sub>-C<sub>4</sub>-haloalkyl and phenoxy,  
phenyl which is disubstituted or trisubstituted by nitro and phenoxy,  
30 phenyl which is trisubstituted by halogen, C<sub>1</sub>-C<sub>4</sub>-alkyl and C<sub>1</sub>-C<sub>4</sub>-alkoxy,  
phenyl which is trisubstituted by halogen, C<sub>1</sub>-C<sub>4</sub>-alkyl and C<sub>1</sub>-C<sub>4</sub>-haloalkyl,  
phenyl which is trisubstituted by halogen, C<sub>1</sub>-C<sub>4</sub>-alkyl and nitro,  
35 phenyl which is trisubstituted by halogen, C<sub>1</sub>-C<sub>4</sub>-alkyl and phenoxy

- phenyl which is trisubstituted by halogen, C<sub>1</sub>-C<sub>4</sub>-alkoxy and C<sub>1</sub>-C<sub>4</sub>-haloalkyl,  
phenyl which is trisubstituted by halogen, C<sub>1</sub>-C<sub>4</sub>-alkoxy and nitro,
- 5 phenyl which is trisubstituted by halogen, C<sub>1</sub>-C<sub>4</sub>-alkoxy and phenoxy,  
phenyl which is trisubstituted by halogen, C<sub>1</sub>-C<sub>4</sub>-haloalkyl and nitro,  
phenyl which is trisubstituted by halogen, C<sub>1</sub>-C<sub>4</sub>-haloalkyl and phenoxy,
- 10 phenyl which is trisubstituted by halogen, nitro and phenoxy,  
phenyl which is trisubstituted by C<sub>1</sub>-C<sub>4</sub>-alkyl, C<sub>1</sub>-C<sub>4</sub>-alkoxy and C<sub>1</sub>-C<sub>4</sub>-haloalkyl,
- 15 phenyl which is trisubstituted by C<sub>1</sub>-C<sub>4</sub>-alkyl, C<sub>1</sub>-C<sub>4</sub>-alkoxy and nitro,  
phenyl which is trisubstituted by C<sub>1</sub>-C<sub>4</sub>-alkyl, C<sub>1</sub>-C<sub>4</sub>-alkoxy and phenoxy,  
phenyl which is trisubstituted by C<sub>1</sub>-C<sub>4</sub>-alkyl, C<sub>1</sub>-C<sub>4</sub>-haloalkyl and nitro,
- 20 phenyl which is trisubstituted by C<sub>1</sub>-C<sub>4</sub>-alkyl, C<sub>1</sub>-C<sub>4</sub>-haloalkyl and phenoxy,  
phenyl which is trisubstituted by C<sub>1</sub>-C<sub>4</sub>-alkyl, nitro and phenoxy,
- 25 phenyl which is trisubstituted by C<sub>1</sub>-C<sub>4</sub>-alkoxy, C<sub>1</sub>-C<sub>4</sub>-haloalkyl and nitro,  
phenyl which is trisubstituted by C<sub>1</sub>-C<sub>4</sub>-alkoxy, C<sub>1</sub>-C<sub>4</sub>-haloalkyl and phenoxy and  
phenyl which is trisubstituted by C<sub>1</sub>-C<sub>4</sub>-haloalkyl, nitro
- 30 and phenoxy.

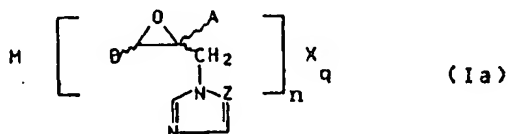
Particularly preferred azolymethyloxiranes I are those in which A is 4-fluorophenyl or 4-chlorophenyl, B is trifluoromethylphenyl and Z is nitrogen.

- Suitable acids for the formation of salts of the
- 35 compounds I are, preferably, halohydric acids, such as hydrochloric acid and hydrobromic acid, in particular hydrochloric acid, which forms particularly readily



crystallizing salts with the compounds I; other suitable acids are phosphoric acid, nitric acid, sulfuric acid, monofunctional and bifunctional carboxylic acids and hydroxycarboxylic acids, such as acetic acid, oxalic acid, maleic acid, succinic acid, fumaric acid, tartaric acid, citric acid, salicylic acid, sorbic acid and lactic acid, and sulfonic acids, such as p-toluenesulfonic acid and 1,5-naphthalenedisulfonic acid.

Acid addition salts are, for example, the chlorides, bromides, sulfates, nitrates, phosphates, oxalates or dodecylbenzenesulfonates. The activity of the salts is due to the cation, so that any anion may be chosen. Metal complexes of the compounds I are compounds of the general formula Ia



where M is a metal, eg. copper, zinc, tin, manganese, iron, cobalt or nickel, preferably copper, X is the anion of an inorganic acid, eg. chloride, sulfate, phosphate or bromide, preferably chloride, and n and q are each 1, 2, 3 or 4, preferably 1 and 2.

The azolylmethyloxiranes of the general formula I can be prepared by the methods described in EP-A-94 564.

The compounds I contain 2 chiral centers and are generally obtained in the form of diastereomer mixtures. These can be separated into the pure diastereomeric enantiomer pairs on the basis of their different physical properties, for example by recrystallization or column chromatography, including HPLC. The said enantiomer pairs can be converted into pure enantiomeric compounds I by known methods for resolving racemates, for example by reaction with a chiral auxiliary component, separation of the resulting diastereomers by one of the abovementioned methods and subsequent elimination of the auxiliary

component, or by column chromatography, including HPLC, over chiral columns packed with, for example, silica gel doped with a solid chiral auxiliary which cannot be washed out.

- 5 The azolymethyloxiranes of the formula I may have a variety of influences on practically all plant development stages, and may therefore be used as growth regulators. The diversity of action of growth regulators depends especially on
- a) the type and variety of plant;
  - 10 b) the time applied, with reference to the development stage of the plant and the time of the year;
  - c) the place and method of application (seed treatment, soil treatment, or foliage application);
  - d) climatic factors, e.g., temperature, amount of precipitate, day length
  - 15 and light intensity;
  - e) soil conditions (including fertilization);
  - f) the formulation of the active ingredient; and
  - g) the concentration at which the active ingredient is applied.
- 20 A description of some of the various possibilities of using the growth regulators according to the invention in agriculture and horticulture is given below.
- A. Vegetative plant growth can be inhibited to a considerable extent, a
- 25 fact which is manifested particularly in a reduction in plant height. The treated plants thus have a compact habit; furthermore, the leaf color is darker.
- Of advantage in practice is for example the reduction in grass growth
- 30 on roadsides, hedges, canal embankments and on areas such as parks, sportsgrounds, fruit orchards, lawns and airfields, thus reducing expensive and time-consuming mowing.
- A further feature of economic interest is the increase in the rigor of
- 35 crops which tend to lodge, such as cereals, Indian corn, sunflowers and soybeans. The shortening and strengthening of the stem thus caused reduces or eliminates the danger of lodging under unfavorable weather conditions.
- 40 The use of growth regulators is also important for inhibiting plant height and changing the time of ripening in cotton. It is thus possible for this important crop to be harvested completely mechanically.

Growth regulators may also increase or inhibit lateral branching. This is of interest when, for instance in tobacco plants, it is desired to inhibit the formation of lateral shoots (suckers) in favor of leaf development.

5

With the compounds of the formula I, it is possible for instance in winter rape to considerably increase the resistance to freeze injury. On the one hand, upward growth and the development of a too luxuriant (and thus particularly frost-susceptible) leaf or plant mass are inhibited; on the other, the young rape plants are kept, in spite of favorable growth conditions, in the vegetative development stage before winter frosts begin. The danger of freeze injury is thus eliminated in plants which tend to lose prematurely their inhibition to bloom and pass into the generative phase. In other crops, too, e.g., winter cereals, it is advantageous if the plants are well tillered in the fall as a result of treatment with the compounds according to the invention, but enter winter with not too lush a growth. This is a preventive measure against increased susceptibility to freeze injury and - because of the relatively low leaf or plant mass - attack by various (especially fungus) diseases. The inhibition of vegetative growth also makes closer planting possible in numerous crops, which means an increase in yield, based on the area cropped.

25 B. Better yields both of plant parts and plant materials may be obtained with the active ingredients according to the invention. It is thus for instance possible to induce increased formation of buds, blossom, leaves, fruit, seed grains, roots and tubers, to increase the sugar content of sugarbeets, sugarcane and citrus fruit, to raise the protein content of cereals and soybeans, and to stimulate the increased formation of latex in rubber trees.

35 The azolylmethyloxiranes of the formula I may raise the yield by influencing plant metabolism or by promoting or inhibiting vegetative and/or generative plant growth.

35

C. It is also possible with the azolylmethyloxiranes I to shorten or lengthen growth stages and to accelerate or retard the ripening process in plant parts either before or after harvesting.

40 A factor of economic interest is for example the facilitation of harvesting made possible by a chemical, temporally concentrated loosening (abscission) of the adherence of stalks to the branches of citrus fruit, olive trees, and other kinds of pomes, drupes and indehiscent fruit. The same mechanism, i.e., promotion of the formation of separation layers between fruit or leaf and stem of the plant, is also essential for a readily controllable defoliation of crop plants, e.g., cotton.

- D. Further, transpiration in crop plants may be reduced with growth regulators. This is particularly important for plants growing in agricultural areas which are expensive to irrigate, e.g., in arid or semi-arid areas. Irrigation frequency can be reduced by using the compounds according to the invention, making for lower costs. As a result of the use of growth regulators, the water available can be better utilized, because, inter alia,
- the size of the stomata opening is reduced;
  - a thicker epidermis and cuticle are formed;
  - penetration of the soil by the roots is improved;
  - the micro-climate in the stand is favorably influenced by the more compact growth.
- 15 The active ingredients to be used in accordance with the invention may be applied not only to the seed (as a disinfectant), but also to the soil, i.e., via the roots, and to the foliage.
- As a result of the good crop plant tolerance, the application rate may vary considerably. When seed is treated, active ingredient amounts of from 0.001 to 50, and preferably from 0.01 to 1, g per kg of seed are generally needed. When the soil or foliage is treated, rates of from 0.01 to 10, and preferably from 0.01 to 5, kg per hectare are generally considered to be sufficient.
- The agents based on the azolylmethyloxiranes I can be employed in the form of conventional formulations such as solutions, emulsions, suspensions, dusts, powders, pastes and granules. The application forms depend entirely on the purposes for which they are intended; they should at all events ensure a fine and uniform distribution of the active ingredient. The formulations are produced in known manner, for example by extending the active ingredient with solvents and/or carriers, with or without the use of emulsifiers and dispersants; if water is used as solvent, it is also possible to employ other organic solvents as auxiliary solvents. Suitable auxiliaries for this purpose are solvents such as aromatics (e.g., xylenes, toluene, benzene), chlorinated aromatics (e.g., chlorobenzenes), paraffins (e.g., crude oil fractions), alcohols (e.g., methanol, butanol), amines (e.g., ethanolamine) N,N-dimethylformamide, and water; solid carriers such as ground natural minerals (e.g., kaolins, aluminas, talc and chalk) and ground synthetic minerals (e.g., highly disperse silica and silicates); emulsifiers such as nonionic and anionic emulsifiers (e.g., polyoxyethylene fatty alcohol ethers, alkyl sulfonates); and dispersants such as lignin, sulfite waste liquors and methylcellulose. It is preferred

to apply the active ingredients according to the invention in aqueous solution, if desired with the addition of water-miscible organic solvents such as methanol or other lower alcohols, acetone, N,N-dimethylformamide or N-methylpyrrolidone.

5

The fungicides generally contain from 0.1 to 95, and preferably from 0.5 to 90, wt% of active ingredient.

The formulations, or the ready-to-use preparations prepared therefrom, 10 such as solutions, emulsions, suspensions, powders, dusts, pastes or granules, are applied in known manner, for example preemergence, post-emergence, or as seed disinfectants.

Examples of formulations are given below.

15

I. 20 parts by weight of compound no. 8 is well mixed with 3 parts by weight of the sodium salt of diisobutyl-naphthalene-sulfonic acid, 17 parts by weight of the sodium salt of a lignin-sulfonic acid obtained from a sulfite waste liquor, and 60 parts by weight of powdered silica 20 gel, and triturated in a hammer mill. By uniformly distributing the mixture in 20,000 parts by weight of water, a spray liquor is obtained containing 0.1% by weight of the active ingredient.

II. 3 parts by weight of compound no. 131 is intimately mixed with 25 97 parts by weight of particulate kaolin. A dust is obtained containing 3% by weight of the active ingredient.

III. 30 parts by weight of compound no. 38 is intimately mixed with a mixture consisting of 92 parts by weight of powdered silica gel and 30 8 parts by weight of paraffin oil which has been sprayed onto the surface of this silica gel. A formulation of the active ingredient is obtained having good adherence.

IV. 40 parts by weight of compound no. 43 is intimately mixed with 10 35 parts of the sodium salt of a phenolsulfonic acid-urea-formaldehyde condensate, 2 parts of silica gel and 48 parts of water. A stable aqueous dispersion is obtained. Dilution in 100,000 parts by weight of water gives an aqueous dispersion containing 0.04% by weight of active ingredient.

40 V. 20 parts of compound no. 43 is intimately mixed with 2 parts of the calcium salt of dodecylbenzenesulfonic acid, 8 parts of a fatty alcohol polyglycol ether, 2 parts of the sodium salt of a phenolsulfonic acid-urea-formaldehyde condensate and 68 parts of a paraffinic mineral oil. A stable oily dispersion is obtained.

VI. 90 parts by weight of compound no. 49 is mixed with 10 parts by weight of N-methyl- $\alpha$ -pyrrolidone. A mixture is obtained which is suitable for application in the form of very fine drops.

5 VII. 20 parts by weight of compound no. 19 is dissolved in a mixture consisting of 80 parts by weight of xylene, 10 parts by weight of the adduct of 8 to 10 moles of ethylene oxide and 1 mole of oleic acid-N-monoethanolamide, 5 parts by weight of the calcium salt of dodecylbenzene-sulfonic acid, and 5 parts by weight of the adduct of 40 moles of ethylene  
10 oxide and 1 mole of castor oil. By pouring the solution into 100,000 parts by weight of water and uniformly distributing it therein, an aqueous dispersion is obtained containing 0.02% by weight of the active ingredient.

VIII. 20 parts by weight of compound no. 8 is dissolved in a mixture  
15 consisting of 40 parts by weight of cyclohexanone, 30 parts by weight of isobutanol, 20 parts by weight of the adduct of 7 moles of ethylene oxide and 1 mole of isooctylphenol, and 10 parts by weight of the adduct of 40 moles of ethylene oxide and 1 mole of castor oil. By pouring the solution into 100,000 parts by weight of water and finely distributing it  
20 therein, an aqueous dispersion is obtained containing 0.02% by weight of the active ingredient.

IX. 20 parts by weight of compound no. 8 is dissolved in a mixture consisting of 25 parts by weight of cyclohexanol, 65 parts by weight of a  
25 mineral oil fraction having a boiling point between 210 and 280°C, and 10 parts by weight of the adduct of 40 moles of ethylene oxide and 1 mole of castor oil. By pouring the solution into 100,000 parts by weight of water and uniformly distributing it therein, an aqueous dispersion is obtained containing 0.02% by weight of the active ingredient.

30 In these application forms, the agents based on the azolylmethyloxiranes I may also be present together with other active ingredients, for example herbicides, insecticides, other growth regulators, and fungicides, and may furthermore be mixed and applied together with fertilizers. Admixture with  
35 other growth regulator mixtures gives synergistic effects, i.e., the action of the combination product is greater than the added actions of its components.

Examples of fungicides which may be combined with the novel compounds are:  
40 sulfur,  
dithiocarbamates and their derivatives, such as  
ferric dimethyldithiocarbamate,  
zinc dimethyldithiocarbamate,

- zinc ethylenebisdithiocarbamate,  
manganese ethylenebisdithiocarbamate,  
manganese zinc ethylenediaminebisdithiocarbamate,  
tetramethylthiuram disulfides,
- 5 ammonia complex of zinc N,N'-ethylenebisdithiocarbamate,  
ammonia complex of zinc N,N'-propylenebisdithiocarbamate,  
zinc N,N'-propylenebisdithiocarbamate and  
N,N'-polypropylenebis(thiocarbamyl) disulfide;  
nitro derivatives, such as
- 10 dinitro(1-methylheptyl)-phenyl crotonate,  
2-sec-butyl-4,6-dinitrophenyl 3,3-dimethylacrylate,  
2-sec-butyl-4,6-dinitrophenyl isopropylcarbonate and  
diisopropyl 5-nitroisophthalate;  
heterocyclic substances, such as
- 15 2-heptadecylimidazol-2-yl acetate,  
2,4-dichloro-6-(o-chloroanilino)-s-triazine,  
O,O-diethyl phthalimidophosphonothioate,  
5-amino-1-[bis-(dimethylamino)-phosphinyl]-3-phenyl-1,2,4-triazole,  
2,3-dicyano-1,4-dithioanthraquinone,
- 20 2-thio-1,3-dithio[4,5-b]quinoxaline,  
methyl 1-(butylcarbaryl)-2-benzimidazolecarbamate,  
2-methoxycarbonylaminobenzimidazole,  
2-(fur-2-yl)-benzimidazole,  
2-(thiazol-4-yl)benzimidazole,
- 25 N-(1,1,2,2-tetrachloroethylthio)-tetrahydrophthalimide,  
N-trichloromethylthiotetrahydrophthalimide,  
N-trichloromethylthiophthalimide,  
N-dichlorofluoromethylthio-N',N'-dimethyl-N-phenylsulfuric acid diamide,  
5-ethoxy-3-trichloromethyl-1,2,3-thiadiazole,
- 30 2-thiocyanatomethylthiobenzothiazole,  
1,4-dichloro-2,5-dimethoxybenzene,  
4-(2-chlorophenylhydrazono)-3-methyl-5-isoxazolone,  
2-thiopyridine 1-oxide,  
8-hydroxyquinoline and its copper salt,
- 35 2,3-dihydro-5-carboxanilido-6-methyl-1,4-oxathiyne,  
2,3-dihydro-5-carboxanilido-6-methyl-1,4-oxathiyne 4,4-dioxide,  
2-methyl-5,6-dihydro-4H-pyran-3-carboxanilide,  
2-methylfuran-3-carboxanilide,  
2,5-dimethylfuran-3-carboxanilide,
- 40 2,4,5-trimethylfuran-3-carboxanilide,  
2,5-dimethyl-N-cyclohexylfuran-3-carboxamide,  
N-cyclohexyl-N-methoxy-2,5-diethylfuran-3-carboxamide,  
2-methylbenzanilide,  
2-iodobenzanilide,

- N-formyl-N-morpholine-2,2,2-trichloroethylacetal,  
 piperazine-1,4-diylbis-(1-(2,2,2-trichloroethyl)-formamide),  
 1-(3,4-dichloroanilino)-1-formylamino-2,2,2-trichloroethane,  
 2,6-dimethyl-N-tridecylmorpholine and its salts,  
 5 2,6-dimethyl-N-cyclododecylmorpholine and its salts,  
 N-[3-(p-tert.-butylphenyl)-2-methylpropyl]-cis-2,6-dimethylmorpholine,  
 N-[3-(p-tert.-butylphenyl)-2-methylpropyl]-piperidine,  
 1-[2-(2,4-dichlorophenyl)-4-ethyl-1,3-dioxolan-2-ylethyl]-1H-1,2,4-  
 -triazole,  
 10 1-[2-(2,4-dichlorophenyl)-4-n-propyl-1,3-dioxolan-2-ylethyl]-1H-1,2,4-  
 -triazole,  
 N-(n-propyl)-N-(2,4,6-trichlorophenoxyethyl)-N'-imidazolyl-urea,  
 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)-butan-2-one,  
 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)-butan-2-ol,  
 15 1-(4-phenylphenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)-2-butanol,  
 $\alpha$ -(2-chlorophenyl)- $\alpha$ -(4-chlorophenyl)-5-pyrimidinemethanol,  
 5-butyl-(2-dimethylamino-4-hydroxy-6-methylpyrimidine,  
 bis-(p-chlorophenyl)-3-pyridinemethanol,  
 1,2-bis-(3-ethoxycarbonyl-2-thioureido)-benzene,  
 20 1,2-bis-(3-methoxycarbonyl-2-thioureido)-benzene,  
 and various fungicides, such as  
 dodecylguanidine acetate,  
 3-[3-(3,5-dimethyl-2-oxycyclohexyl)-2-hydroxyethyl]-glutaramide,  
 hexachlorobenzene,  
 25 DL-methyl-N-(2,6-dimethylphenyl)-N-fur-2-yl alanate,  
 methyl DL-N-(2,6-dimethylphenyl)-N-(2'-methoxyacetyl)-alanate,  
 N-(2,6-dimethylphenyl)-N-chloroacetyl-DL-2-aminobutyrolactone,  
 methyl DL-N-(2,6-dimethylphenyl)-N-(phenylacetyl)-alanate,  
 5-methyl-5-vinyl-3-(3,5-dichlorophenyl)-2,4-dioxo-1,3-oxazolidine,  
 30 3-[3,5-dichlorophenyl]-5-methyl-5-methoxymethyl-1,3-oxazolidine-2,4-dione,  
 3-(3,5-dichlorophenyl)-1-isopropylcarbamyldantoin,  
 N-(3,5-dichlorophenyl)-1,2-dimethylcyclopropane-1,2-dicarboximide,  
 2-cyano-[N-(ethylaminocarbonyl)-2-methoximino]-acetamide,  
 1-[2-(2,4-dichlorophenyl)-pentyl]-1H-1,2,4-triazole,  
 35 2,4-difluoro- $\alpha$ -(1H-1,2,4-triazol-1-ylmethyl)-benzhydrol alcohol.

#### Manufacturing example

##### I. Manufacture of the precursors

40

##### 2-Bromomethyl-2-phenyl-3-(2-chlorophenyl)-oxirane

30 g of 1-(2-chlorophenyl)-2-phenyl-3-bromoprop-1-ene was refluxed  
 with 23 g of 3-chloroperoxybenzoic acid in 500 ml of chloroform. Upon



completion of the reaction, the chloroform phase was washed free of acid with aqueous sodium bicarbonate solution and water, dried over sodium sulfate and evaporated down under reduced pressure. From the residue there was obtained 41.3 g (70.2%) of 2-bromomethyl-2-phenyl-3-(2-chlorophenyl)-oxirane, which was then processed further.

## II. Manufacture of the end products

### 2-(1,2,4-Triazol-1-ylmethyl)-2-phenyl-3-(2-chlorophenyl)-oxirane

10

At room temperature, a solution of 32 g of 2-bromomethyl-2-phenyl-3-(2-chlorophenyl)-oxirane in 150 ml of N,N-dimethylformamide was added to a suspension of 23 g of 1,2,4-triazole and 5 g of sodium hydride (80% dispersion in mineral oil) in 150 ml of N,N-dimethylformamide.

15

After 8 hours, the reaction solution was poured into water and extracted with ethyl acetate. The organic phase was washed with water and dried over sodium sulfate, and the solvent was stripped off under reduced pressure. The diastereomer mixture which formed was subjected to incipient crystallization from methyl tert-butyl ether to give 15 g of cis-2-(1,2,4-triazolyl-1-ylmethyl)-2-(phenyl)-3-(2-chlorophenyl)-oxirane of melting point 150°C. From the mother liquors there was obtained 6.3 g of trans-2-(1,2,4-triazolyl-1-ylmethyl)-2-(phenyl)-3-(2-chlorophenyl)-oxirane of melting point 117°C.

20

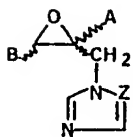
25 The compounds I listed in the table below may be readily obtained from appropriate starting materials in accordance with the above manufacturing example; their action is expected to be similar. The nomenclature "cis" or "trans" isomer relates to the position of the azole to the radical B with regard to the C-C bond of the oxirane ring.

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Table



(I)

Compound 5 No.	A	B	Z	Isomer	mp [°C]
1	phenyl	2-chlorophenyl	N	cis	159
2	4-chlorophenyl	2-chlorophenyl	N	cis	166
3	4-diphenyl	2-chlorophenyl	N	cis	191
10 4	2,4-dichlorophenyl	2-chlorophenyl	N	cis	resin
5	2-chlorophenyl	2-chlorophenyl	N	cis	
6	2-fluorophenyl	2-chlorophenyl	N	cis	145-147
7	4-tolyl	2-chlorophenyl	N	cis	140
8	4-fluorophenyl	2-chlorophenyl	N	cis	136
15 9	3-bromo-4-fluorophenyl	2-chlorophenyl	N	cis	129-130
10	4-bromophenyl	2-chlorophenyl	N	cis	
11	3,4-dichlorophenyl	2-chlorophenyl	N	cis	
12	4-tert.-butylphenyl	2-chlorophenyl	N	cis	122
13	3-chlorophenyl	2-chlorophenyl	N	cis	
20 14	3,5-dichlorophenyl	2-chlorophenyl	N	cis	
15	4-phenoxyphenyl	2-chlorophenyl	N	cis	
16	4-tert.-butylphenyl	2-chlorophenyl	CH	cis	123
17	4-fluorophenyl	2-chlorophenyl	CH	cis	119-122
18	4-fluorophenyl	2-chlorophenyl	CH	trans	resin
25 19	4-fluorophenyl	2-chlorophenyl	N	trans	resin
20	2-fluorophenyl	2-chlorophenyl	CH	cis	87
21	4-chlorophenyl	2-chlorophenyl	CH	cis	90- 92
22	phenyl	2-chlorophenyl	CH	cis	85- 87
23	4-chlorophenyl	2-fluorophenyl	N	cis	140
30 24	phenyl	2-fluorophenyl	N	cis	139
25	2-fluorophenyl	2-fluorophenyl	N	cis	128
26	2,4-dichlorophenyl	2-fluorophenyl	N	cis	resin
27	4-fluorophenyl	2-trifluoromethylphenyl	N	cis	110-112
28	phenyl	4-fluorophenyl	N	cis	73
35 29	4-fluorophenyl	2-trifluoromethylphenyl	CH	cis	133-135
30	4-fluorophenyl	2,4-dichlorophenyl	N	cis	127
31	4-fluorophenyl	3-chlorophenyl	N	cis	resin
32	4-fluorophenyl	3-chlorophenyl	CH	cis	resin

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Compound No.	A	B	Z	Isomer	mp [°C]
5	33 4-chlorophenyl	2-chloro-4-fluorophenyl	CH	cis	132
	34 4-chlorophenyl	2-chloro-4-fluorophenyl	N	cis	143-145
	35 phenyl	2-chloro-4-fluorophenyl	CH	cis	117
	36 phenyl	2-chloro-4-fluorophenyl	N	cis	123
	37 4-fluorophenyl	2-chloro-4-fluorophenyl	CH	cis	135
10	38 4-fluorophenyl	2-chloro-4-fluorophenyl	N	cis	139
	39 4-fluorophenyl	phenyl	N	cis	89- 92
	40 2-fluorophenyl	2-fluorophenyl	CH	cis	79- 82
	41 phenyl	4-trifluoromethylphenyl	CH	cis	106
	42 phenyl	4-trifluoromethylphenyl	N	cis	132
15	43 4-chlorophenyl	4-trifluoromethylphenyl	N	cis	135
	44 4-chlorophenyl	4-trifluoromethylphenyl	CH	cis	123
	45 2,4-dichlorophenyl	3-fluorophenyl	CH	cis	125
	46 4-fluorophenyl	4-bromophenyl	N	cis	119
	47 4-fluorophenyl	3-fluorophenyl	N	cis	99
20	48 4-fluorophenyl	4-fluorophenyl	N	cis	69
	49 4-chlorophenyl	2-chloro-6-fluorophenyl	N	cis	150
	50 phenyl	4-bromophenyl	N	cis	122
	51 phenyl	2-chloro-6-fluorophenyl	N	cis	158
	52 4-tolyl	2-fluorophenyl	N	cis	127
25	53 4-fluorophenyl	2-fluorophenyl	N	cis	114
	54 3-bromo-4-fluorophenyl	2-fluorophenyl	N	cis	106
	55 4-diphenyl	2-fluorophenyl	N	cis	
	56 2-chlorophenyl	2-fluorophenyl	N	cis	
	57 4-bromophenyl	2-fluorophenyl	N	cis	
30	58 3,4-dichlorophenyl	2-fluorophenyl	N	cis	
	59 4-tert.-butylphenyl	2-fluorophenyl	N	cis	
	60 3-chlorophenyl	2-fluorophenyl	N	cis	
	61 3,5-dichlorophenyl	2-fluorophenyl	N	cis	
	62 4-phenoxyphenyl	2-fluorophenyl	N	cis	
35	63 phenyl	2-bromophenyl	N	cis	153
	64 4-bromophenyl	phenyl	CH	cis	152-153
	65 4-bromophenyl	4-chlorophenyl	CH	cis	143-144
	66 phenyl	2,4-dichlorophenyl	CH	cis	103
	67 4-bromophenyl	2,4-dichlorophenyl	CH	cis	107-108
40	68 2,4-dichlorophenyl	4-chlorophenyl	CH	cis	135

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Compound No.	A	B	Z	Salt	Isomer	mp [°C]
69	4-chlorophenyl	phenyl	CH		cis	138
5 70	4-bromophenyl	2,4-dichlorophenyl	N		cis	133-134
71	methyl	2,4-dichlorophenyl	CH		cis	113-117.5
72	methyl	2,4-dichlorophenyl	CH		trans	98-104
73	tert.-butyl	4-chlorophenyl	N		cis	79- 86
74	tert.-butyl	4-chlorophenyl	CH	HCl	cis	214-216
10 75	tert.-butyl	phenyl	N	HCl	cis	148
76	tert.-butyl	phenyl	CH		cis	75
77	tert.-butyl	2,4-dichlorophenyl	N		cis	124
78	tert.-butyl	2,4-dichlorophenyl	CH		cis	95
79	4-chlorophenyl	4-tert.-butylphenyl	CH		trans	160-162
15 80	4-chlorophenyl	4-tert.-butylphenyl	N		cis	176-177
81	2,4-dichlorophenyl	4-tert.-butylphenyl	CH		cis	132-134
82	methyl	2,4-dichlorophenyl	N		cis	105-108
83	methyl	2,4-dichlorophenyl	N		trans	80- 85
84	methyl	2,4-dichlorophenyl	N		cis/trans	70- 81
20					=1:1	
85	4-tert.-butylphenyl	4-chlorophenyl	CH		cis	100-102
86	4-tert.-butylphenyl	4-chlorophenyl	N		cis	105-107
87	4-tert.-butylphenyl	2,4-dichlorophenyl	CH		cis	101-113
88	4-tert.-butylphenyl	2,4-dichlorophenyl	N		cis	108-111
25 89	4-chlorophenyl	3-methoxyphenyl	CH	HCl	cis	173
90	4-chlorophenyl	3-methoxyphenyl	N		cis	77
91	phenyl	2,4-dichlorophenyl	N		cis	159-161
92	4-chlorophenyl	3-trifluoromethylphenyl	CH		cis	101-104
93	4-chlorophenyl	3-trifluoromethylphenyl	N		cis	107-109
30 94	phenyl	3-trifluoromethylphenyl	CH		cis	77-78.5
95	phenyl	3-trifluoromethylphenyl	N	HCl	cis	131-133
96	phenyl	phenyl	CH		cis	108-110
97	4-chlorophenyl	4-fluorophenyl	CH		cis	130-132
98	phenyl	4-chlorophenyl	CH		cis	105-106
35 99	phenyl	phenyl	N		cis	116-118
100	phenyl	4-chlorophenyl	N		cis	114-115
101	4-chlorophenyl	phenyl	N		cis	106-110
102	4-diphenyl	4-chlorophenyl	N		cis	163-165
103	4-bromophenyl	phenyl	N		cis	115-120
40 104	4-bromophenyl	4-chlorophenyl	N		cis	115-120
105	4-chlorophenyl	4-fluorophenyl	N		cis	112-117
106	4-chlorophenyl	4-bromophenyl	N		cis	115-119
107	4-chlorophenyl	4-bromophenyl	CH		cis	114-116

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Compound No.	A	B	Z	Salt	Isomer	mp [°C]
108	4-chlorophenyl	4-bromophenyl	CH		trans	179-181
5 109	2,4-dichlorophenyl	4-bromophenyl	CH		cis	135-139
110	4-chlorophenyl	4-fluorophenyl	N		trans	219-223
111	4-chlorophenyl	4-bromophenyl	N		trans	210-213
112	2,4-dichlorophenyl	4-bromophenyl	N		cis	108-110
113	2,4-dichlorophenyl	phenyl	CH		cis	resin
10 114	2,4-dichlorophenyl	phenyl	CH		trans	118-121
115	2,4-dichlorophenyl	phenyl	N		cis	resin
116	4-benzenesulfonyl-phenyl	4-chlorophenyl	CH		cis	193-195
117	4-benzenesulfonyl-phenyl	4-chlorophenyl	CH		trans	204-205

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Compound No.	A	B	Z	Metal complex	Isomer	mp [°C]
118	4-benzenesulfonylphenyl	4-chlorophenyl	N		cis	132-135
5 119	4-benzenesulfonylphenyl	4-chlorophenyl	N		trans	175-177
120	2-naphthyl	2,4-dichlorophenyl	CH		cis	135
121	2-naphthyl	2,4-dichlorophenyl	N		cis	151
122	4-chlorophenyl	4-chlorophenyl	CH		cis	115-120
123	4-chlorophenyl	4-chlorophenyl	N		cis	105-108
10 124	2-naphthyl	4-chlorophenyl	CH		cis	140
125	2-naphthyl	4-chlorophenyl	N		cis	107
126	2,4-dichlorophenyl	4-tert.-butylphenyl	CH		trans	142-143
127	3,4-dichlorophenyl	4-bromophenyl	N		cis	130-134
128	4-bromophenyl	phenyl	CH	1/2 CuCl	cis	198-200
15 129	4-chlorophenyl	2-chlorophenyl	N	1/2 CuCl <sub>2</sub>	cis	155
130	4-fluorophenyl	2-chlorophenyl	N	1/2 CuCl <sub>2</sub>	cis	175
131	4-chlorophenyl	2-fluorophenyl	N	1/2 CuCl <sub>2</sub>	cis	145
132	phenyl	2-chlorophenyl	N	1/2 CuCl <sub>2</sub>	cis	210

## Use examples

To determine the growth-regulating properties of the candidate compounds, a culture medium was supplied with sufficient nutrients, and test plants 5 were grown therein in plastic pots approx. 12.5 cm in diameter and having a volume of about 500 ml.

In the preemergence treatment, the candidate compounds were poured onto the seedbed as aqueous formulations on the day of sowing. In the post-10 emergence treatment, the candidate compounds were sprayed onto the plants as aqueous formulations.

The growth-regulating action observed was confirmed at the end of the experiment by height measurements. The figures obtained were compared with 15 those for untreated plants.

Not only was growth height reduced - the leaves also took on a more intense color. The increased chlorophyll content is indicative of a higher rate of photosynthesis, making for bigger yields.

20

The substance used for comparison purposes was 2-chloroethyltrimethyl-ammonium chloride (CCC).

Table 1

25

Spring barley, "Aramir" variety; preemergence (soil) treatment

Compound No.	Concentration in mg of compound/vessel	Relative growth height
30 untreated	-	100
CCC	6	86.1
27	6	25.7
43	6	43.1

35 Table 2

Lawnseed "Tiergarten Mischung"; postemergence (leaf) treatment

Compound No.	Concentration in mg of compound/vessel	Relative growth height
40 untreated	-	100
CCC	1.5	104.1
	6	104.1
43	1.5	65.8
	6	38.4

Table 3

Sunflowers "Sorex" variety; postemergence (leaf) treatment

5	Compound No.	Concentration in mg of compound/vessel	Relative growth height
	untreated	-	100
	CCC	6	84.7
	8	6	63.5
10	19	6	77.6
	43	6	64.0
	131	6	71.8

Table 4

15

Spring rape "Petranova" variety; postemergence (leaf) treatment

	Compound No.	Concentration in mg of compound/vessel	Relative growth height
20	untreated	-	100
	CCC	6	89.3
	4	6	69.1
	7	6	76.0
	8	6	70.6
25	27	6	69.1
	30	6	81.7
	34	6	72.2
	43	6	80.2
	49	6	72.2
30	131	6	71.9

## 2. Rice seedling test

35 Young rice seedlings (Bahia variety) were cultivated in a nutrient solution containing the active ingredients in various concentrations. After cultivation for six days at 25°C in permanent light the active ingredient concentration was determined at which the length of the second sheath is decreased by 50 % (= KI<sub>50</sub>).

40 (W. Rademacher and J. Jung, Berichte aus dem Fachgebiet Herbologie ("Reports from the herbology field"), vol. 24, pp 127-134, University of Hohenheim, 1983).



Compound No.	KI <sub>50</sub> (molar)
CCC	$1.5 \times 10^{-2}$
7	$1.8 \times 10^{-5}$
5 8	$1.3 \times 10^{-6}$
17	$6.5 \times 10^{-6}$
19	$6.0 \times 10^{-5}$
30	$6.4 \times 10^{-6}$
33	$8.9 \times 10^{-6}$
10 34	$2.8 \times 10^{-6}$
35	$3.2 \times 10^{-5}$
36	$7.3 \times 10^{-6}$
37	$1.5 \times 10^{-5}$
38	$1.2 \times 10^{-6}$
15 47	$1.1 \times 10^{-6}$
48	$8.1 \times 10^{-7}$
49	$3.0 \times 10^{-6}$

### 3. Improving the yield in barley

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Spring barley of the Aura variety was grown in 5 liter Mitscherlich vessels in a sandy loam to which sufficient nutrients had been added. Each vessel contained 14 plants. All the plants had been treated several times with fungicides to prevent fungal infection and thus substantially

25 eliminate falsification of the results. The plants were cultivated in the open, protection merely being given against inclement weather conditions.

At a growth height of approx. 38 cm, the plants were sprayed uniformly with an aqueous formulation of an azolylmethyloxirane I (3.1 ml/vessel).

30 The yields are given in the Table below and show that for example compound no. 8 results in a significant increase in yield. It can be concluded from the way in which this experiment was carried out that the increase in yield is not attributable to a fungicidal action of the candidate compounds or to the avoidance of lodging.

35

Compound No.	Appln. rate (mg of compound/vessel)	Yield [%] (Control = 100%)
8	5	120
8	10	111
40 8	15	118

